

ON MECHANICAL AND MAGNETIC FACTORS INFLUENCING
THE ORIENTATION AND PERFECTION OF BISMUTH
SINGLE-CRYSTALSBY ALEXANDER GOETZ
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ABSTRACT

Method of producing crystals of bismuth.—A method is described which permits the production of single crystals of metals, with practically no limit to size or to desired orientation, thus indicating that all external mechanical influences are avoided. Furthermore, the method permits the zone of formation in a growing crystal to be subjected to a strong magnetic field.

Mechanical factors influencing the orientation and perfection of crystals.—A systematic study of the conditions in which the seed-crystal transfers its orientation to the rod is made. Experiments with artificially distorted seeds, etc., show that crystalline units must already exist in the liquid state. It is shown that this "liquid crystal" is destroyed at about 10° above the melting point. It is suggested that these units are identical with elementary units of a crystal as treated theoretically by Zwicky and observed by the author.

The influence of a magnetic field on a forming crystal.—Crystals in the three main orientations to the directions of the field lines (20,000 Gauss) were grown, one-half with, the other half without field. No change in the orientation between both halves could be observed as long as no secondary influence was present. However, crystals grown without a predetermined orientation indicated a preference for an orientation in which the direction of the smallest diamagnetic susceptibility (along the trigonal axis) was parallel to the lines of force. The fact that this influence, though much smaller than the orienting forces of a seed, exists, supports the assumption of "block-phase" slightly above the melting point.

INTRODUCTION

THERE are several reasons why a systematic investigation of the factors influencing the orientation and perfection of a metal crystal seems to be important. One of these reasons is the fact that certain methods of growing crystals succeed only for certain orientations, though the orientation is forced on the growing crystal by inoculation with a seed-crystal. Then it can happen that the desired orientation is only maintained over a short region or does not even start. In a previous paper,¹ Goetz and Hasler came to the same conclusion as Kapitza:² namely, that a growing crystal is very sensitive to any mechanical stress. Such stresses exist in almost every known method of crystal production. This necessitates the development of a new method which allows also the decision to be made as to whether this extremely sensitive region is in the solid part of the growing crystal or in the still liquid state.

A. Goetz and Maurice F. Hasler, *Proc. Nat. Acad.* **15**, 646 (1929).

² P. Kapitza, *Proc. Royal Soc.* **A119**, 358 (1928).

Furthermore, it seemed to be interesting to see if directional forces of other than mechanical or thermal, especially magnetic, nature would show any influence when applied to the zone of formation. In spite of several papers written on this subject, no investigations excluding secondary effects have been systematically made. The results correlated from these papers contradict each other to some extent also.

THE METHOD OF PRODUCING CRYSTALS

After investigating the conditions for an unrestricted growth of Bi crystals by means of all known methods, it was found that these conditions can be summarized as follows:

- (1) No strain of any kind should be applied to the zone of formation of the growing crystal.
- (2) The crystal should not have any oxide-coat which can be the cause of stress.
- (3) The speed of growth should be uniform.
- (4) The heat gradient over the crystal should be uniform and its position within the crystal constant over the whole length.
- (5) If the orientation of the crystal is to be predetermined by inoculation, it is necessary to obtain thermal equilibrium at the transition between seed-crystal and inoculated metal.

There is no method known which fulfills all these conditions equally well. However Kapitza's method, with which he produced the crystals finally used for his measurements, comes nearest, but it cannot be used for long crystals and does not satisfy condition (2).

Condition (1) seemed to me the most important one, and a large number of experiments were performed to fulfill it satisfactorily. One of the main troubles was that the molten metal (as soon as it was free from oxide) stuck to the walls of the container, thus interfering with the change of volume at crystallization. Many different arrangements were tried. For instance, a trough of thin paper was made in which the molten Bi was poured. When heated the paper carbonized, yet kept its shape sufficiently until the metal crystallized. The strength of these troughs was so small that the crystallizing metal could break them easily. Very uniform crystals were obtained by this method but the external shape was quite irregular. Finally, it was found that smooth troughs of Acheson graphite worked as well as the troughs of carbonized paper without having the disadvantage of losing their shape after the crystallization of the metal.

The final arrangement based on the previous experiences was the following: The troughs were shaped out of large blocks of Acheson graphite from a region free from fissures. The troughs had a length of 30 cm, were 0.4 cm wide and shaped rectangularly. Special precautions had to be observed in shaping to avoid deformations caused by the flexibility of the material. To fulfill condition (2) it was necessary to place the trough *G* in a glass or quartz tube *C* (in Fig. 1) which had at one end a ground-glass cone in which a little glass dome with a capillary was fitted. The cross-section of *C* was circular

over the whole length to within 3 cm of the cone, where it was as shown in the cross section (Fig. 1) elliptical to give more space above the trough. *F* was an electric furnace (chromel wire coiled around a quartz-tube) with two end plates, through the holes of which went the tube *C*, in such a manner that it did not touch the walls. The tube was supported at one end by means of the V-shaped adjustable holder *A* in which the tube glided over graphite wedges. The other end of the tube was supported at the clamp *O* which was a part of the driving arrangement fulfilling condition (3) (not shown in Fig. 1, because its design has already been published¹.) The connection between *O* and *C* was made with a rubber-tube *N* which absorbed to some extent the vibrations of the motor.

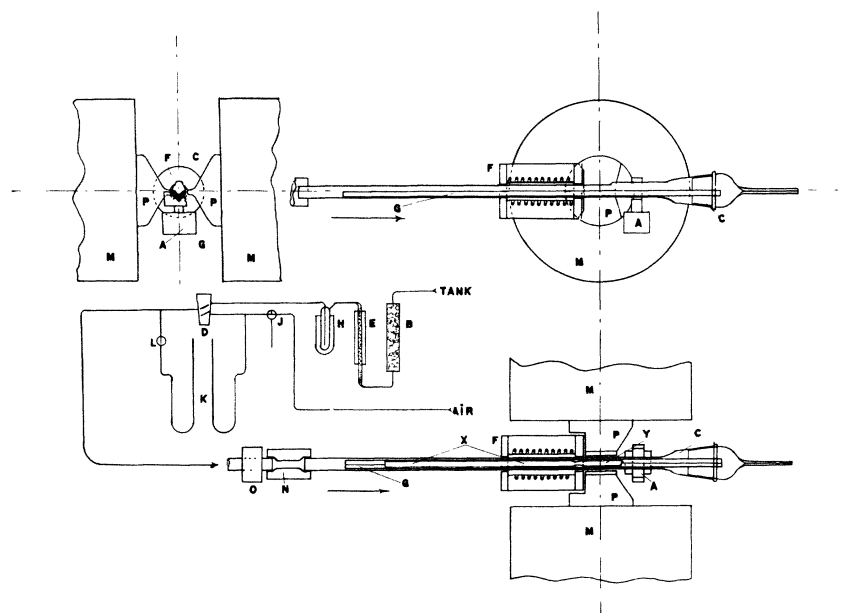


Fig. 1. Diagram of essential features of the apparatus.

The method of producing crystals was as follows: Round metal rods of 2–3 mm diameter were first made in glass tubes as described in another paper.¹ After the glass was taken off, the rods were cut down to a standard length of 120 mm (first generation).

The clamp *O* was then disengaged from the driving mechanism and moved towards the right so that the tube *C*, and with it the trough *G*, came out of the furnace *F* as far as possible. The glass dome was then removed and the rod placed in the trough. Then the tube was closed and the clamp *O* was put back into such a position that the end of the rod came out of the furnace *F* for a short distance. The furnace was restrictively heated so as not to melt the end of the rod. After the tube had come to thermal equilibrium with the furnace, the clamp *O* was engaged with the driving apparatus which moved

it in the direction of the arrow at a rate of 5 mm/min. To reduce the oxide at the surface of the rod a constant flow of hydrogen was sent through the tube. It soon became apparent that the purity of the hydrogen and the constancy of the flow were of great importance for the uniformity of the crystals, which made a rather elaborate arrangement necessary. The hydrogen was first taken from a tank with a reduction valve. To separate dust from the gas, it was then sent through a gas filter *B* and then through a heated tube with palladiumized asbestos to oxidize the impurities; thereafter through the trap *H*, cooled by liquid air, and then through the valve *D*. From here it went into the tube, over the metal and escaped through the capillary in the dome. The rate of flow could be measured by one of the manometers *K*.

By this arrangement, it was possible to keep the thickness of the oxide coat over the whole length of the crystal practically constant, since the factors determining the rate of reduction, temperature (very important), flow of hydrogen, and speed of the trough through the furnace could all be controlled. It soon became apparent that a perfect reduction is highly undesirable, because as soon as the last surface layer is gone, the surface tension of the liquid metal becomes so large that it coagulates into large drops and thus destroys entirely the uniform cross-section of the crystal. This effect made it necessary to provide an arrangement which permitted the production of a very thin oxide layer over the crystal. For this purpose, compressed air was used, which went first through the valve *J*, then through the stopcock *D* which opened the way to *C* either for the hydrogen or the air. For making the change between these two gases as fast as possible, every unnecessary apparatus-volume not exposed to the direct flow was avoided. Therefore, the hydrogen manometer, for instance, could be closed with the stopcock *L* as soon as the air-flow, which was measured by the manometer *K* (right), started.

For producing the "second generation," the rod was placed in the trough, as mentioned above, and the furnace heated to about 310°. To prevent coagulation, the first few millimeters were placed so that they did not melt, then the hydrogen flow was turned on at a pressure of 20–25 mm water-column and the motor started. Thus the metal rod melted into the shape of the trough and was reduced so that the surface became very bright. As soon as the other end of the rod entered the furnace the hydrogen-flow was stopped and the air-flow started to cover this part with an almost invisible coat which fixed the shape of the end of the rod and thus prevented the metal from running forward under the influence of surface tension.

This second generation was, in general, monocrystalline, but the orientation was at random. To predetermine the orientation the method of inoculation by a seed-crystal was used. For this purpose, the metal rod obtained by the previous methods was placed again in the trough, the latter being placed in the furnace, again under a flow of hydrogen, so as to melt the right end of the rod. The thin oxide-coat kept the end in shape, since the temperature (about 290°) of the furnace was so low that no appreciable reduction occurred. As soon as the end was liquid (Fig. 2a), the glass dome of *C*

was removed, a hooked steel needle was introduced and the oxide coat taken off the end of the liquid rod (Fig. 2b). The hydrogen flow prevented a re-oxidation of this point, whereas the oxide-hull of the rest kept the rod in shape. Then the seed-crystal, the end of which was cleaved immediately before using, was brought into the trough (Fig. 2c). The liquid end of *X* and the left end of *Y* were brought into contact very carefully, so that they united over a small region (Fig. 2d). Again coagulation had to be avoided by pulling the seed-crystal out a trifle so as to produce a little constriction between *X* and *Y*. (Fig. 2e). The glass dome of *C* was then replaced, the tube itself pushed back into the furnace for annealing the transition (Fig. 2f) and the hydrogen-flow was replaced by an air-flow. This process was necessary in order to protect the very delicate junction between *X* and *Y* by a uniform oxide coat (see later). After the rod and the seed-crystal reached

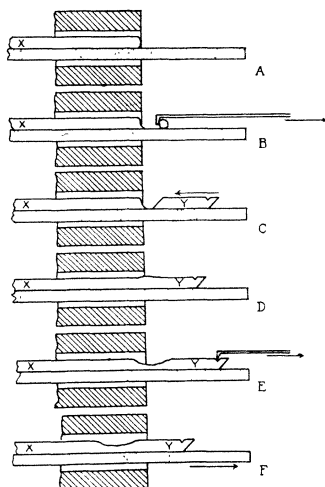


Fig. 2. Method of inoculating rod with seed crystal.

thermal equilibrium, corresponding to the new position in the furnace, the motor was started and thus the crystal started to grow. As soon as the junction came out of the furnace, the air flow was replaced by hydrogen to prevent a thickening of the oxide coat on *X*. It was found that this oxide coat had to be very thin, almost invisible to the eye, and had to be very uniform over the whole rod. For fulfilling this condition, it was necessary to start the hydrogen rather exactly at the moment at which the junction started to crystallize. The moment at which the air inside *C* was replaced by hydrogen could easily be observed on account of the difference of viscosity of the two gases. The storage pressure of the hydrogen indicated by the manometer *K* (left) was large as long as the rest of the air had to flow through the capillary of *C*, but went down to a constant value as soon as the tube contained only hydrogen. The opposite was the case if the hydrogen was replaced by air.

Thus the third generation of the crystal was obtained. After the whole rod crystallized, it was taken out of the trough very carefully and etched with diluted nitric acid. If all precautions had been observed carefully, the crystal obtained was perfectly uniform in shape and orientation, and not the smallest alien crystal could be observed. The orientation of the crystal was

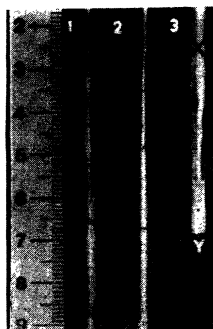


Fig. 3. Crystal 1 shows first "generation" after removing the glass cover. It is polycrystalline and shows many regions of twinning. Crystal 2 is second "generation," its core being singly-crystalline. However, its surface contains many crystals in twin orientations due to oxide stress. Crystal 3 is third "generation" (X) with the seed-crystal (Y) in orientation P_1 . The rod is a single crystal.

exactly the one of the seed crystal, no matter which orientation that had. It was found also that this method had no limitations in the matters of the lengths and the cross-sections of the crystal. Fig. 3 shows a photograph of the first three generations of crystals.

As has been mentioned above, the whole investigation was undertaken to study the factors influencing the orientation and perfection of these

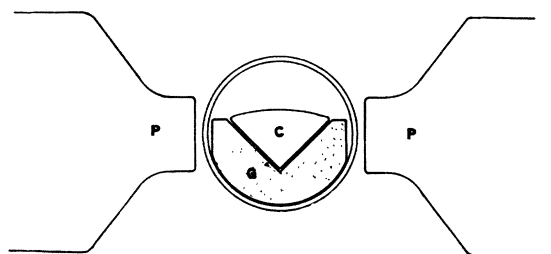


Fig. 4. Cross-section of arrangement for crystallization in a magnetic field.

crystals with special regard to the influence of a transverse magnetic field. The method just described allowed a very exact location of the zone in which the crystal formed. If the temperature of the furnace was high enough, this zone was outside the furnace; hence it was possible to bring it between the pole-pieces of an electromagnet M . The pole-pieces P were shaped so as to concentrate the field between two edges and thus across the crystal over a

length of 18 mm. This distance was necessary to allow for the unavoidable uncertainty in the exact position of the zone of formation. Fig. 4 shows an enlarged cross-section of the arrangement whereas Fig. 5 is a top view photograph which shows the crystal *C* lying in the trough *G* as it comes out of the furnace *F* and crystallizes between the pole pieces *P* of the magnet *M*.

This method has the disadvantage that the direction of the lines of force cannot be changed relative to the rod. Nevertheless, it is possible to change the orientation in the rod by inoculation with different seed crystals. This allowed the study of the influence of the field at different angles with regard to the trigonal axis.

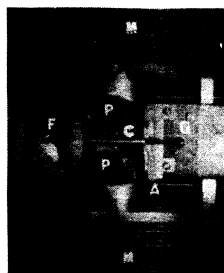


Fig. 5. Top view of the formation of the single crystal *C* carried in the trough *G* between the pole pieces *PP* of the magnet *M* after being molten in the furnace *F*.

MECHANICAL FACTORS INFLUENCING THE ORIENTATION AND PERFECTION OF CRYSTALS

For studying the kinds of influences preventing a perfect growth of Bicrystals, about 500 crystals were grown under circumstances which were changed systematically. The results concerning the disturbances involved in the artificial growth by inoculation can be summarized as follows.

Two different kinds of mischief in the production of single crystals have to be separated, (a) the fact that the rod consists of several crystals with different orientations, and (b) the fact that the inoculation of the rod by a seed-crystal does not succeed. All experiments were performed at a constant speed (exact to about 0.2 percent), in absence of vibration, and at a constant temperature (exact to 2°).

The failure of an inoculation can consist of

- (1) That the orientation of the rod has no relation whatsoever to the seed crystal;
- (2) That the orientation of the rod is partly the same as the seed crystal;
- (3) That the orientation of the rod is the twin orientation of the seed crystal.

The first case occurred in general if the contact between rod and crystal was bad. It was quite remarkable how an almost invisible layer of oxide between both parts destroyed entirely the influence of the seed crystal,

although they may have congealed and formed a unit after solidification. Case (2) can have the same cause as (1). If the face of contact between both parts was partly contaminated by oxide, then one half grew in the orientation of the seed crystal, whereas the other half, separated from the seed by contamination, formed one or several new centers of crystallization which produced new crystals which grew together with the inoculated one. There may be still another cause which will be discussed later. The most interesting case is (3). Here one can have a perfect crystal, the orientation of which is the same throughout, only that the perfect cleavage of the seed plane is replaced by one of the imperfect cleavage planes. The same effect may occur in case (2), where one can obtain the parallel growth of two crystals with interchanged planes.

It is well known that almost any deformation in a Bi crystal results in the production of twin-lamellae^{3,4} where the (111) plane is replaced by one of



Fig. 6.

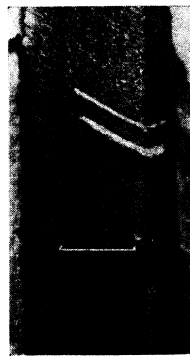


Fig. 7.

Twin lamellae caused by distortion in Bi single crystals. The illumination under the microscope was such as to show the original orientation of the crystal dark (Fig. 7) or bright (Fig. 6). The white line in Fig. 7 corresponds to 1 mm.

the $(11\bar{1})$ type. The change takes very little energy because the rhombohedral symmetry of Bi is almost a cubic one. Fig. 6 and Fig. 7 illustrate this effect on two artificially distorted crystals of Bi, which show the appearance of the twin lamellae differently illuminated. Thus the conclusion is easily reached that the twinning occurred in case (3) at the point where seed and rod came in contact. A close investigation of this effect brought out the following facts.

If the seed-crystal is not perfect, i. e. if it contains twin lamellae which are easily observed under the microscope after etching (3) the rod will grow frequently in the twin orientation. It is furthermore very hard to avoid the twinning effect if one cleaves crystals in special orientations, as was shown by x-ray diagrams, but it is possible by careful handling to extend the twinned region not farther than a few tenths of a mm beyond the cleaved plane. Thus

³ P. Mügge, *Jahrbuch d. Mineralogie* **1**, 183 (1886).

⁴ A. Goetz, *Proc. Nat. Acad.* in press.

in order to inoculate the rod with an undisturbed seed, it is only necessary to bring the trough, after the contact between rod and seed is made (Fig. 2 e) far enough into the furnace so that the imperfect end of the seed is melted (Fig. 2 f). Then the unhurt part of the seed reinoculates its imperfect part and the rod starts to crystallize in the desired orientation.

However, it was very surprising that case (3) occurred very often, even though this precaution was taken, i.e. the rod crystallized in the twin orientation in spite of a perfect seed.

Closer investigation showed that this effect had two reasons. One should expect that if one inoculates with well twinned seed crystals i.e. where distinct regions of the crystal have either the normal or the twin orientation as shown in Fig. 6 and 7, one would obtain rods of both orientations depending on the position of the point up to which the seed was melted. But it was discovered that *the rod grows in an orientation possessed by a region of the seed which was already molten*. This process is shown schematically in Fig. 8 where X is the molten rod and Y the seed crystal having the twin-lamellae $t, t \dots$. In case the seed Y was molten up to point 1, X grew in the orientation corresponding to the seed. If Y was molten up to point 2, X grew in the twin orien-

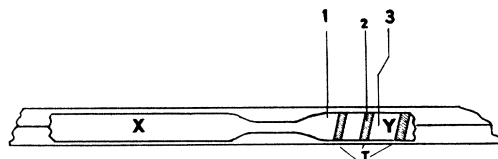


Fig. 8.

tation. But if Y was liquidified up to point 3, where the twin lamella was doubtlessly melted, X grew still in the twin orientation. This experiment could be repeated as often as desired. The maximum distance still effective between the border of the lamella and the end of the molten region was, in general, several millimeters. Fig. 9 shows an enlarged photograph of the transition between seed and rod. The illumination of the crystal is such as to show the parts of the desired orientation bright. The dark crystal is the seed (right) which shows three good intersections of twin lamellae. The white half to the left is the beginning of the inoculated rod, which shows the same orientation as the twin lamellae of the seed-crystal. The sharp transition shows how far the seed was melted. The original end of the seed had one twin lamella which was melted about 0.5 mm beyond its left border, but was still able to determine the orientation of the rod. The faint black lines on the left crystal are twin lamellae in the rod which were produced later to show that they have the original orientation of the seed indicated by their dark appearance.

This phenomenon shows that the forces determining the orientation of a crystal are not destroyed at the melting point and exist within the liquid as long as the temperature is near to that of the melting point.

The study of the conditions of successful inoculation with untwinned crystals (or seeds melted far beyond the limits of the imperfections) revealed

another phenomenon which points in the same direction. As mentioned above it was necessary (to preserve the perfect shape of the rod) to pull the seed a little away from the rod (Fig. 2 d) so that the junction was constricted (Fig. 2 e). It goes without saying that this constriction concerned only the region where the metal was molten entirely. It was found, nevertheless, in almost all cases, that the rod grew in the twin orientation of the seed if the crystallization was started from the position of the trough in Fig. 2 e. After the crystal was finished, it was etched and the region where the twin orientation occurred could be determined easily. It started always close to point 1 (Fig. 4 e) i.e. at the beginning of the constriction, no matter whether the melted region of the seed reached still farther or not.

The only way to avoid this twinning effect in the liquid was to anneal the liquid junction at temperatures much higher than the melting point; hence the



Fig. 9. Seed crystal with twin lamellae (right), inoculated crystal (left) grew in twin orientation although the twinned region of the seed was molten. The white line corresponds to 1 mm.

trough had to be backed into the furnace (Fig. 2 f) and kept in that position for 5-7 minutes before the crystallization was started.

This effect shows that within the temperature region of the "liquid crystal," the twinning occurs just as well as in the solid state with the only difference that the little energy necessary for changing the shape of the liquid rod (determined by its surface tension and the shape of the thin oxide cover) is already sufficient to produce the effect.

The fact that the orientation of a crystal is not destroyed immediately after melting could be shown in another experiment. If a polycrystalline rod (first generation) was put into the trough and was run through the furnace with the usual speed, but a maximum temperature which was only slightly above the melting point, a polycrystalline rod was obtained which had the same position and the same orientation of the different prominent crystal elements as it had before it entered the furnace although it had been molten and recrystallized. As soon as the temperature was higher, an entirely different polycrystalline combination occurred.

The high sensitivity to any stress applied to the transition between solid and liquid metal causes another effect which is highly undesirable. If a single crystal rod which is covered by oxide was placed in the trough and pulled through the furnace, a rod was generally obtained which was monocrystalline at the core but polycrystalline at the surface, an observation which was also made by Kapitza². Under the microscope, it was observed that the alien crystals have the shape of thin stripes running along the rod, each of them starting at a wrinkle in the oxide coat produced by the shrinking of the metal at the moment of melting. As soon as the rod crystallized, these wrinkles were stretched out again, but the pressure necessary for this process was sufficient to cause twinning if the oxide coat was sufficiently thick. The alien crystals produced by this cause were only at the surface and could be removed by etching. The effect was different if the rod was free from oxide and the oxide coat was produced around the rod in the molten state. Then the whole hull was too small for the solid form and it had to be split by the solidifying metal, which caused pressures which were very often able to start an entirely new orientation. Hence it was necessary to grow the metal in a reducing atmosphere so that the oxide coat was too thin to affect the structure of the crystal, but sufficient to preserve the shape of the molten rod.

With regard to the orientation which is produced by these stresses, the following can be said: Any tension longitudinal with regard to the rod results in an orientation in which the trigonal axis is normal to the rod. If the original orientation is already such, the tension has no influence at all. If the stresses are not very large, the new orientation is obtained by twinning which places the trigonal axis in a direction in which the energy needed for overcoming the obstacles of thermal contraction is smaller. This is the reason as already stated in another paper,¹ crystals, the trigonal axes of which are parallel to the rods, are very difficult to obtain with the usual methods, which apply either longitudinal tensions or lateral compressions to the zone of formation due to the expansion of the metal at the moment of crystallization. The method described avoids these influences and allows the growth of all possible orientations equally well. However, the opposite effect can be shown, where a longitudinal compression prevents the perfect growth of a crystal, the axis of which is normal to the rod. If a rod was covered with a heavy oxide coat and inoculated with a seed, the axis of which was normal to the rod, the last end of the rod had an orientation in which the axis became more parallel to the rod. The obvious reason is that the oxide at the end of the rod formed a kind of sack, the end of which prevented the longitudinal expansion and thus exerted a longitudinal compression, which resulted in an orientation of maximum contraction parallel to it.

THE INFLUENCE OF THE MAGNETIC FIELD UPON THE CRYSTALLIZATION.

Since the orientation and perfection of these crystals could be influenced mechanically when in the molten state, it seemed worth while to study whether or not a magnetic field applied to the zone of formation would produce any effects.

The way in which the magnetic field was applied has already been described. The tests were made as follows: The crystal (third generation), with an already definite orientation, was put into the trough and the tube pulled back into the furnace so far that the left end of the crystal did not melt. The temperature of the furnace was increased so much that the transition between liquid and solid crystal was approximately at the middle of the pole pieces when the crystal reached its thermal equilibrium, a process which took in general, 5 minutes. Then the magnetic field was excited and the driving mechanism started at the same time. Thus the molten part of the rod crystallized again within a transversal magnetic field of a strength of 20,000-21,000 gauss.

It is obvious that there are three different possible orientations of the crystal with respect to the rod, or to the direction of the lines of force. These orientations which differ fundamentally are as sketched in Fig. 10. This

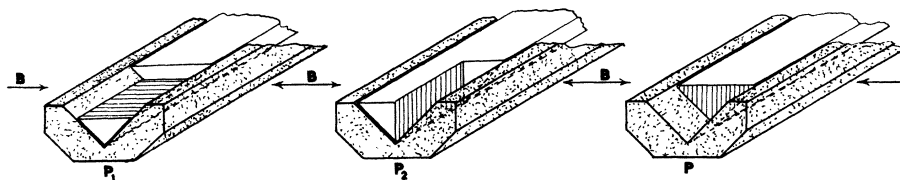


Fig. 10.

shows the trough G (dotted) with the crystal, the latter cut parallel to its main cleavage plane. These three main orientations are:

Name	Trigonal axis to rod field		(111) plane to rod field	
P_1	\perp	\perp	\parallel	\parallel
P_2	\perp	\parallel	\perp	\perp
P_3	\parallel	\perp	\parallel	\parallel

As long as the conditions of growth were not influenced accidentally, *no influence of the magnetic field upon the crystallographic orientation could be observed, no matter which of the above main orientations was introduced into the field.* It is to be mentioned however, that this result can only be obtained if one succeeds in avoiding any secondary influence. Any shock, for instance caused by the sudden excitation of the magnet, transferred to the trough or to the furnace will immediately produce a change in orientation.

Moreover, crystals, the orientation of which had not been predetermined, were grown in a magnetic field to find out whether there exists an influence of the field on the first originating center of crystallization. In fact, indications were found which point toward a preference of an approximate parallelism of the trigonal axis and the lines of force. However, these results seem not to be precise enough for a definite statement, since first the number of measured crystals produced this way was not large enough that the results could be considered statistically; and second, it is known that the direction of the

heat-gradient with relation to the rod can predetermine the orientation aside from any mechanical influence. Thus, the non-inoculated crystal may not have been entirely free to grow in any orientation because the apparatus did not allow a change of the direction of the heat-gradient with respect to the rod. On the other hand, it is certain that these predetermining influences are extremely small because they cannot affect, in any way, the growth of an inoculated crystal. However, the influence of the applied field showed itself to be smaller than the orienting forces of an inoculating crystal and may be similar in magnitude to the orienting forces of the gradient, which makes it possible that the effects produced by the latter fog the former.

DISCUSSION

The results obtained by the above observations may be able to explain a number of experiences of other authors. It has been already suggested in a previous paper¹ that the extended experiments of Hoyem and Tyndall⁵ on single zinc crystals may find their explanations in the effect of the stress applied to the zone of formation by the weight of the liquid column hanging from the crystal. The variation of the successfulness of an inoculation with the temperature of the molten metal can thus be explained, because the length of the liquid column depends upon that temperature and herewith its weight.

Moreover the lack of success of several methods of Kapitza² and his explanation thereof is confirmed and becomes understandable as soon as one realizes that in the case of liquid bismuth, the interchange of the main cleavage plane with an $(11\bar{1})$ plane is exactly the effect which occurs in any plastic deformation of solid bismuth. It seems that there are only two alternate interpretations possible: First, one could assume that the twinning force of the crystal becomes infinitely small in the neighborhood of the melting point so that the smallest strain, as given, for instance, by the surface tension of the liquid metal, is sufficient to start the twinning; or second, in view of the observed facts one might assume that the twinning effect occurs within the melted region, which would mean that the crystal is not destroyed entirely after melting, but that it consists still of units which preserve their orienting power. The first makes it impossible to explain the fact that qualities can be "inherited" by a growing crystal from the molten region of a seed crystal or to explain the preservation of a polycrystalline structure in a bar heated above the melting point. These units exist apparently only over a small range of temperature, since the phenomena through which one infers their presence disappear entirely about 10° above the melting point (annealing of the liquid metal).

One is perhaps not entirely wrong in assuming that these units are of the of the same nature as the "blocks" in a Bi-crystal described by the author in a recent paper¹ in connection with the theoretical considerations of Zwicky.⁶ In this case, one considers that the melting crystal disintegrates first into its

⁵ A. G. Hoyem and E. P. T. Tyndall, *Phys. Rev.* **33**, 81 (1929).

⁶ F. Zwicky, *Proc. Nat. Acad.* **15**, 253, 000 (1929).

blocks which exist within a state of equilibrium of dissociation with the liquid metal at each temperature. This "block phase," however, exists only over a small range of temperature.

There are several indications in experiments of other authors which are in favor of this hypothesis. Boydston⁷ found in observing the thermal e.m.f. of Bi-crystals of different orientations that the e.m.f.'s characteristic for the crystalline state did not disappear exactly at the melting point, but continued for a few degrees. Thus (to quote his own words) "it appears, in fact, as if some crystalline arrangement still persists in the molten metal"

Futhermore, Traube and vonBehren have shown⁸ that the dissolving of a crystal into an almost saturated solution results in separating particles of ultra-microscopic size from the crystal, "submicrons," which exist for a considerable length of time. The parallelism between the melting process and the process of dissolving into a saturated solution does not need to be mentioned.

Finally, it is possible to connect the observations by Stewart and his collaborators⁹ concerning the "cybotactic" state of matter with these results. It seems as if there is no principal difference between the "block-phase" and the "cybotaxis."

Regarding the extremely small energy needed for influencing the orientation in a liquid crystal, I was surprised to find no orientating effect caused by the magnetic field on a crystal with a predetermined orientation. This however, does not contradict necessarily, experiments which were performed by Plücker¹⁰ and Leduc.¹¹ From experiments on polycrystalline Bi solidified in a magnetic field, Plücker finds that among the individual crystals, one direction is predominant, that is where the trigonal axis is parallel to the lines of force. A result of this kind should be expected, if there is any positive effect, because of the anisotropic diamagnetism of Bi, as the trigonal axis is known to be parallel to the most "paramagnetic" direction. The observations of Leduc¹¹ point in the same direction. He crystallized Bi in spherical glass containers which could be suspended within a field of 4-5000 Gauss. These Bi balls were polycrystalline without doubt, but suspended in the field they turned into a direction in which the "average main axis" of the conglomerate was parallel to the lines of force. If the ball was formed outside the field, no prediction about its zero position in the field could be made, but as soon as the sphere had crystallized within the field, the zero position was the same as its position during the crystallization. The explanation of this effect is obviously the same as of Plücker's observations, although, the orientation of the conglomerate was not measured by Leduc.

It seems surprising that Welo did not find any effect of this kind in a recent study.¹² It may be due to the fact that his way of casting his disk in a

⁷ R. W. Boydston, *Phys. Rev.* **30**, 911 (1927).

⁸ J. Traube and W. von Behren, *Sx. f. Phys. Chem.* **A138**, 85 (1928).

⁹ G. W. Stewart and R. M. Morrow, *Phys. Rev.* **30**, 232 (1927).

¹⁰ S. Plucker, *Pogg. Ann.* **76**, 583 (1849).

¹¹ M. A. Leduc, *C. R.* **140**, 1022 (1905).

¹² L. A. Welo, *Phys. Rev.* **34**, 296 (1929).

mould with good thermal conductivity produced a polycrystallization so rapid that the orienting effect was very small.

Our own observations make a directional effect, in a crystal which crystallizes completely in a magnetic field, probable with a sign which agrees with Plücker's and Leduc's experiments. They show, however, that this effect is so small that it cannot overcome the orienting forces of a seed-crystal.

The presence of the magnetic effect shows furthermore, that the orientation of a crystal must exist already in the liquid state provided that the crystal unit has still freedom to move with regard to the rod. This supports again the existence of the above "block-phase." The insensibility of the inoculated crystal shows further that the growing crystal, if under stable conditions, must have an already ordered section of the liquid ahead of it. Then the orienting effect of a magnetic field is too small to break up the liquid arrangement.

Nevertheless, it was found that the magnetic field influences considerably other properties of a Bi crystal formed in it, as stated already by the author and his collaborators^{13, 14, 15}. More extensive results will be published soon.

I feel very much indebted to Dr. R. A. Millikan for the interest he showed in this investigation, and I should like to express my thanks to my assistants, Mr. M. F. Hasler and Mr. A. B. Focke for their very helpful assistance.

¹³ A. Goetz, *Phys. Rev.* **32**, 322 (1928).

¹⁴ A. Goetz and M. F. Hasler, *Phys. Rev.* **34**, 549 (1929).

¹⁵ A. Goetz, R. C. Hergenrother and A. B. Focke, *Phys. Rev.* **34**, 546 (1929).

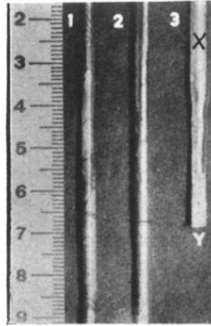


Fig. 3. Crystal 1 shows first "generation" after removing the glass cover. It is polycrystalline and shows many regions of twinning. Crystal 2 is second "generation," its core being singly-crystalline. However, its surface contains many crystals in twin orientations due to oxide stress. Crystal 3 is third "generation" (X) with the seed-crystal (Y) in orientation P_1 . The rod is a single crystal.

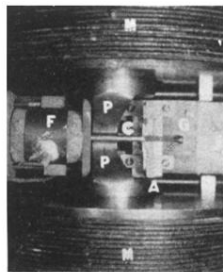


Fig. 5. Top view of the formation of the single crystal C carried in the trough G between the pole pieces PP of the magnet M after being molten in the furnace F .



Fig. 6.



Fig. 7.

Twin lamellae caused by distortion in Bi single crystals. The illumination under the microscope was such as to show the original orientation of the crystal dark (Fig. 7) or bright (Fig. 6). The white line in Fig. 7 corresponds to 1 mm.

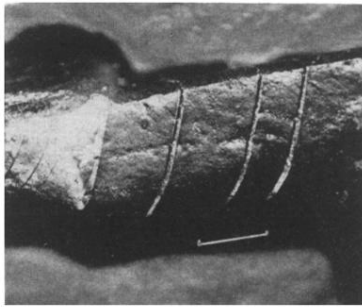


Fig. 9. Seed crystal with twin lamellae (right), inoculated crystal (left) grew in twin orientation although the twinned region of the seed was molten. The white line corresponds to 1 mm.